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**TOWARD QUANTITATION OF ION/MOLECULE KINETICS IN FOURIER
TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY**

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ABSTRACT

The effects of excitation amplitude, collisional relaxation of ions, and incomplete ejection of unwanted ions, on the individual and total ion intensities in a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer have been studied. These effects are found to be in general agreement with existing theories of ion motion in FTICR analyzer cells. The influence of these factors on determination of rate coefficients for ion/molecule reactions is discussed.

INTRODUCTION

While considerable effort has been expended in determining exact peak positions (masses) [1] and peak heights (intensities) [2,3] using FTICR mass spectrometry [4], far less attention has been paid to factors which might affect the values of ion/molecule reaction rate coefficients obtained with the technique. In this paper we examine three different factors which can significantly influence the quantitation of ion/molecule reaction rate coefficients: the amplitude of the excitation which excites ions into coherent



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motion just prior to the FTICR detection process, collisional relaxation of ions along the z-axis into the center of the FTICR cell, where detection efficiencies are highest, and incomplete ejection of unwanted ions from the FTICR cell.

It has often been noted in FTICR mass spectrometry that careful "tuning" is necessary in order to obtain proper relative peak "intensities", for example, those reflecting known naturally occurring isotopic abundances. Such tuning involves optimizing the amplitude, sweep rate, and sweep range of the most commonly applied type of excitation, the frequency "chirp". Severe mass discrimination can be produced by improper tuning, with either high or low mass ions favored depending on excitation level. Figure 1 shows this effect for some low-mass carbon cluster ions which have been produced by direct laser vaporization of graphite. As seen in the Figure, higher excitation amplitudes (lower attenuations) favor higher mass ions, and vice versa. The exact cause of this discrimination has not been identified definitively, but it may in part be related to the kinetic energy of the ions and their position in the ICR cell before and/or after excitation. The calculation of ICR detection efficiency and signal strength as a function of ion location for different cell geometries has been summarized by Dunbar [5]. A theory has also been developed by Rempel et al. [6] which accounts for the effect of z-axis oscillation amplitude of a trapped ion on its induced signal. However, no mass dependence for the effects considered is predicted in either case. Two papers discussing the excitation of z-axis motion by frequencies slightly higher than the cyclotron frequency, ω_{eff} [7], and by excitation at twice the trapping frequency, $2\omega_T$, and $2\omega_T + \omega_{\text{eff}}$ [8] have recently appeared. The general mass discrimination illustrated in Figure 1 cannot be explained by the results of either of these papers. Three-dimensional ion motion modelling studies [9]

may lead to a better understanding of the factors involved in this phenomenon. It has also been suggested [9] that application of the stored waveform, inverse Fourier transform ("SWIFT") excitation method can eliminate this problem.

While optimization of excitation parameters can often improve the qualitative appearance of FTICR mass spectra, one must still be extremely careful in obtaining certain types of quantitative data. This is particularly true when determining ion/molecule reaction rate coefficients. If the intensity of a single ion is followed as a function of reaction time, a mass discrimination effect should cause little problem, particularly if the precautions noted by Rempel et al. [6] are followed. However, given the ability of FTICR mass spectrometers to obtain complete mass spectra at varying reaction times, ion intensities normalized with respect to the sum of all the ICR peak heights or areas are often used for kinetics studies. If mass discrimination is present, and relatively high mass ions are being formed from those of relatively low mass, erroneous rate coefficients can be obtained.

The effect of an ion's position in the cell along a coordinate parallel to the magnetic field axis (commonly designated the z-axis) on its detection efficiency has been discussed [6]. Detection efficiency is reduced as an ion moves farther from the center of the cell and closer to the trapping plates which are designed to constrain the ion's motion along the z-axis. Significant collisional relaxation of ions along the z-axis toward the center of the cell can occur during the long reaction times employed in ion/molecule reaction studies, resulting in an increase in the total ion intensity as a function of time. The effect of cell geometry on the coupling of radial and axial motions has also been discussed [7]. An increase in the total ion intensity, particularly if it is compounded by the mass dependent detection

efficiency noted above, can significantly affect the determination of ion/molecule reaction rate coefficients.

To simplify ion/molecule kinetics studies, ions whose intensities are not being followed as a function of reaction time are often ejected after ion formation from the cell using the FTICR double resonance technique [10]. Care must be taken to eject unwanted ions without imparting excess kinetic energy to the ion under study from the "tail" of the ejection frequency used. However, if insufficient ejection voltages are employed, ions may merely be excited to orbits with large radii and remain in the cell. They may then be finally ejected by the (relatively low amplitude) frequency sweep used as part of the FTICR detection scheme. If sufficient time is given between the initial, supposed, ejection of these ions and the detection process (as will often be the case in ion/molecule kinetics studies), some ions which have not quite been ejected from the cell will undergo collisional relaxation, resulting in smaller cyclotron radii. The FTICR excitation/detection process will not eject these ions, and they will appear to be the products of ion/molecule reactions, increasing in intensity as a function of reaction time.

This paper reports a quantitative study of the three factors mentioned above, with recommendations as to experimental methods of minimizing their effect on ion/molecule reaction rate studies.

EXPERIMENTAL

Experimental conditions used for excitation and detection in these experiments (in a one inch cubic cell) were the default parameters of the Nicolet FT/MS-1000 data system [11], i.e., sweep rate of 2.667 kHz/ μ s, ion mass range detected from 17.274 to 2,997 amu, ions of frequency from 0 to

2.667 MHz excited, and a detection bandwidth of 2.667 MHz, except that 16 K rather than 8 K data points were collected. Time-domain signals were apodized with a modified Blackman-Harris function [12], and zero-filled once prior to Fourier transformation. A 5 ms pulse of 50 eV electrons was used for ionization, with ca. 500 nA emission current.

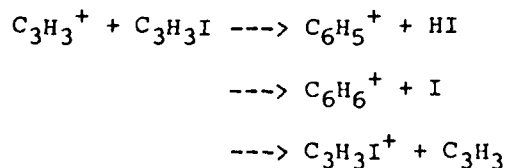
All chemicals were obtained commercially [13] and purified by repetitive freeze pump thaw cycles except propargyl iodide, which was prepared from propargyl chloride by a halogen exchange reaction [14]. The details of synthesis and purification are given elsewhere [15].

Two different magnets were used during the course of this study. The first was a superconducting magnet with a magnetic field of 3 Tesla and the second was an electromagnet which was operated at 1 Tesla. An ionization gauge was used for all pressure measurements and pressures in this paper are reported without correction. Details of typical FTICR experimental sequences can be found elsewhere [4].

RESULTS AND DISCUSSION

A. Effect of Excitation Level on the Intensity of Ions of Different Mass.

The reaction of $C_3H_3^+$ with propargyl iodide, the neutral molecule from which $C_3H_3^+$ was formed by charge transfer with Xe^+ , was studied using a Nicolet FT/MS-1000 mass spectrometer with a magnetic field of 3 Tesla. The primary ion/molecule reactions which occur during the 200 ms reaction time and at 8×10^{-8} torr pressure of propargyl iodide are [15]:



The effect of excitation amplitude on the total ion signal (magnitude-mode

peak area of the 5 major peaks: $C_3H_3^+$, $C_6H_5^+$, $C_6H_6^+$, $C_9H_7^+$ and $C_3H_3I^+$) for 3 and 200 ms reaction times is shown in Table 1.

Table 1 shows that the ratio of total ion peak area (as defined above) at 200 ms reaction time to that at 3 ms reaction time increases with increasing excitation amplitude. If this effect were the same for collisionally relaxed ions of all masses, ion/molecule reaction rate coefficients could still be calculated by normalizing individual ion peak areas with respect to total ion signal. However, Table 2 and Figure 1 show that this is not the case. As the excitation amplitude is increased, the area of higher mass ions increases dramatically relative to that of lower mass ions. Similar trends were seen for the intensity ratios of intermediate mass ions. The direction of frequency sweep (low to high or high to low) had no significant effect on these ratios.

For this reaction sequence, as is usually the case in ion/molecule reaction studies, higher mass ions are produced from lower mass ones. At longer reaction times, as higher mass ions are produced from lower mass ions, higher excitation amplitudes, which favor higher mass ions, will cause the apparent total ion signal to increase. With such a mass discrimination effect present, a normalization factor which depends on the peak areas of different masses will give incorrect normalized single ion peak areas for the determination of ion/molecule reaction rate coefficients. However, it is possible to select an excitation level ($15 V_{p-p}$ in this case) which gives a total ion signal which does not change with time and thus leads to proper normalization factors and more reliable rate coefficient data. This optimum excitation level will vary with sweep rate and range, and needs to be significantly less [7] than that which will produce an ICR orbit whose diameter is of the order of the trapped-ion cell dimensions.

Recently it has been suggested [9] that in addition to suitable sweep rate and excitation levels, higher trapping voltages also help keep the total ion intensity constant. This procedure may be satisfactory for isotope ratio measurements, but for kinetic studies one usually prefers to use lower trapping voltages, in order to avoid trapping ions with high kinetic energies.

Persistence of this mass discrimination under different experimental conditions (as is mentioned above) implies that the excitation mechanism used in this study, i.e., chirp excitation, could be the source of this discrimination. It has been suggested (but not yet reported in print) that application of the constant-phase stored waveform, inverse Fourier transform ("SWIFT") excitation method can minimize this problem.

B. Effect of Pressure on Ion Intensities

A study of the effect of excitation voltage on total and individual ion peak areas at different pressures indicates that there exists an optimum pressure at which the total ion signal stays constant with time and at which the ratio of the peak area of the highest mass ion to that of the lowest mass ion also has the least fluctuation. For the experiment whose results are reported in Tables 1 and 2, a total pressure of 2×10^{-6} torr gave the best results. For experiments carried out at different pressures a different optimum excitation level would have to be determined.

Such a pressure effect is due to at least two opposing factors. During ion formation and reaction times collisions cause ions formed near the trapping plates to be relaxed toward the center of the cell and therefore the apparent total ion signal increases. An increase in pressure or reaction time (up to the limit at which ion loss from the cell becomes a dominant factor) increases this collisional relaxation process. On the other hand, during the

excitation and detection period collisions can disturb the coherent motion of the ions and therefore reduce the detected total ion peak area. Figure 2 shows the effect of "reaction time" and pressure on the area of the $C_6H_6^+$ peak. For this study benzene cations were produced by impact of ca. 10 eV electrons in a magnetic field (produced by an electromagnet) of 1 Tesla and constrained by a trapping voltage of two volts. As a function of reaction time the $C_6H_6^+$ peak area increases to a maximum and then decreases due to ion loss from the cell. At higher pressures the rate of increase in peak area is faster and therefore the plateau region is reached sooner. These results are consistent with relaxation of ions along the z-axis of the cell proposed earlier [6].

In order to minimize these pressure effects the use of a ramped trapping voltage [6] and a pulsed valve to introduce an inert collision gas at short reaction times is recommended. Preliminary results employing pulsed valves in our laboratory, however, show that such experiments must be accompanied by high pumping speed in order to reduce the total pressure to its initial value on a time scale no greater than that on which the ion/molecule reactions to be studied are taking place. An external ion source or a dual cell with higher pressure in the ion source and lower pressure in the analyzer region would also reduce such pressure effects.

C. Effect of Incomplete Ejection on Ion Intensities

In order to obtain the most unambiguous results in ion/molecule reaction studies, it is desirable to isolate the ion of interest by using FTICR ejection capabilities. The rate coefficient is then measured by monitoring the decrease of the signal for the single remaining ion as a function of reaction time. If the amplitude of the signal used for ejection is not sufficiently

high some "ejected" ions may be translationally excited to larger radii and may not be ejected initially. With short delay times (in which few collisions take place), these ions can be ejected during the ion excitation which preceeds FTICR detection. With longer delay (reaction) time between "ejection" and detection, ion signals will increase due to collisional relaxation of ions originally formed by the electron beam but not efficiently ejected and coupling of axial and radial motion [6,7]. This effect is shown in Figure 3. When an rf ejection pulse with an amplitude of ca. $6 V_{p-p}$ was used, (bottom curve), ions were completely ejected from the cell. However, the top curve in Figure 3 shows a less favorable condition. At short delay times, a few percent of the ions were detected because the low ejection pulse amplitude did not completely eject all of the ions. In this case, no signal was seen for most of the ions because they were actually ejected during the excitation which preceeds FTICR detection. At longer delay times about 50 percent of the ions (the ion intensity in the absence of ejection was 350 based on the scale of the Figure 3) were retained in the cell due to the effects described above.

The effect of this incomplete ejection of the unwanted ions will not only be the false identification of these ions as the products of an ion/molecule reaction but also an increase in the total ion signal with increasing delay times and therefore erroneous normalization factors and rate coefficient values. By decreasing the amplitude of excitation for detection at short delay (reaction) times, one can determine the point at which the unwanted ions are no longer completely ejected from the cell in the desired fashion, and operate at an ejection amplitude above that level.

This effect is not limited solely to the "ejected" ions. Ions close to those being ejected will also be affected by the ejection pulse if proper ex-

citation levels have not been used. Figure 4 shows this effect for benzene cations, m/z 78, (produced as described above), when m/z 79, the ^{13}C isotope of the benzene cation, was ejected from the cell with different ejection amplitudes. As is shown, at high ejection voltage amplitudes most of the $^{12}\text{C}_6\text{H}_6^+$, m/z 78, ions were also ejected from the cell. Under these conditions only a few percent of the C_6H_6^+ , m/z 78, ions which were excited to the higher orbits and supposedly ejected are not actually ejected during the excitation for detection and thus are seen at longer reaction times.

At an excitation voltage of $6.2 V_{p-p}$ (lowest curve in Figure 4) almost all of the adjacent, m/z 78, ions have also been ejected from the cell and only ca. 2.5% of these ions, which were excited to larger radii but not ejected, are detected at longer times. Only at an excitation voltage of $2.1 V_{p-p}$, (top curve in Figure 4) does the behavior of the signal for m/z 78 as a function of time approach that seen with no ejection of adjacent ions in Figure 2. It is clear that best results can be obtained when the minimum power necessary for complete ejection is used, and that experiments to check that ejected ions do not "reappear" as a function of reaction time are needed. Use of lower ejection voltage for longer irradiation periods will produce a narrower frequency-domain excitation power spectrum and therefore decrease the energy transferred to ions with m/z close to ejected ions.

D. Other Effects

The effects described above are also dependent on cell structure. The reported results were obtained in a cell modified for laser irradiation of trapped ions, with 1 cm diameter holes covered by copper mesh in the excitation plates. Different optimum excitation levels were obtained when a cell with solid plates was used. The same trends were observed with the latter

cell, but fluctuations of the total ion intensity with excitation level were less than with the cell containing "mesh-covered" holes in the excitation plates.

A comparison of the results obtained using an electromagnet-based FTICR with a magnetic field of 1 Tesla and those using a superconducting magnet-based FTICR with a magnetic field of 3 Tesla shows that the effect of ejection signal on the adjacent ions and therefore on the total ion signal is more dramatic for the electromagnet. This could be due to both the poorer homogeneity and the lower magnetic induction of this magnet. Since the separation between the cyclotron frequencies of two ions increases with magnetic field, power absorption of the adjacent ions for carefully tailored ejection pulses will be less of a problem when using the higher field superconducting magnet.

CONCLUSION

A number of experimental parameters must be optimized when determining ion/molecule reaction rate coefficients using FTICR techniques. For each value of the total pressure, the excitation amplitude must be optimized so that the total ion signal remains constant with reaction time. Ramped trapping voltages and/or use of pulsed values to introduce a buffer gas should be employed to relax ions rapidly to the center of the cell prior to kinetic studies. Ejection of unwanted ions should be done with sufficient excitation amplitudes to insure that the ions are completely ejected from the cell. Care must be taken in tailoring the ejection pulses (or the SWIFT technique should be used) to avoid exciting the ion whose ion/molecule kinetics are being studied.

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3. "Intensity" in other forms of spectroscopy is a measure of power absorption, and is proportional to the number of absorbing species. Peak height (in ICR or elsewhere) is not. We have chosen to use the magnitude-mode peak area, as determined by a Nicolet algorithm which sums the values of all discrete data points in a peak above a certain threshold value, as a spectral measure of the relative number of ions. Although magnitude-mode area is theoretically unbounded for a Lorentzian line shape, in practice for thresholds set at the experimental noise levels, the algorithm gives peak areas which have proven suitable for quantitation in these and other experiments, as long as sufficient data points are present so that the peak in question is defined by > ca. 15 points. We are grateful to a referee for clarifying this matter.
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Table 1. Effect of excitation amplitude on total ion intensity.

Excitation voltage (V_{p-p})	Attenuation, db	Total ion signal* with 3 ms delay time(I_1)	Total ion signal* with 200 ms delay time(I_2)	I_2/I_1
15	10	211	208	0.99
17	9	223	248	1.11
19	8	234	282	1.21
22	7	242	315	1.30
24	6	250	350	1.40
27	5	240	375	1.56
30	4	210	385	1.83
34	3	161	378	2.35
37	2	137	375	2.74
45	0	51	177	3.47

* As defined in text, arbitrary units, total pressure = 2×10^{-6} torr
(ionization gauge, uncorrected).

Table 2. Effect of excitation amplitude on the lowest and highest mass ions.

Excitation voltage (V_{p-p})	Peak area* of the lowest mass ion ($C_3H_3^+$), after 200 ms	Peak area* of the highest mass ion ($C_3H_3I^+$), after 200 ms	$I_{C_3H_3I^+}/I_{C_3H_3^+}$
15	43	26	0.60
17	51	38	0.75
19	54	42	0.78
22	60	48	0.80
24	65	54	0.83
27	66	59	0.85
30	63	65	1.03
34	54	71	1.31
37	46	77	1.67
45	10	60	6.00

* Arbitrary units, total pressure = 2×10^{-6} torr.

FIGURE CAPTIONS

- Figure 1. Effect of excitation level on low and high mass carbon cluster ions. $\lambda = 532$ nm and laser pulse energy of ca. 10 mJ/pulse.
- Figure 2. Effect of reaction time and pressure on $C_6H_6^+$ ion peak area. $\square = 2 \times 10^{-7}$ torr, $+$ = 8×10^{-7} torr and $\diamond = 1.6 \times 10^{-6}$ torr.
- Figure 3. Effect of amplitude of the ejection pulse on the $C_6H_6^+$ ion signal. Excitation voltages (V_{p-p}) for \square , $+$, \diamond , Δ , \times and ∇ were 6.2, 5, 3.1, 2.6, 1.1 and 0.84 volts, respectively. Resonant excitation for 1 ms was used, with $p = 3 \times 10^{-7}$ torr.
- Figure 4. Effect of m/z 79 ejection pulse amplitude on m/z 78 ions. Excitation voltages (V_{p-p}) for \square , $+$, \diamond , Δ , \times and ∇ were 6.2, 5, 4, 3.1, 2.6 and 2.1 volts, respectively. Resonant excitation for 1 ms was used, with $p = 2.5 \times 10^{-7}$ torr.

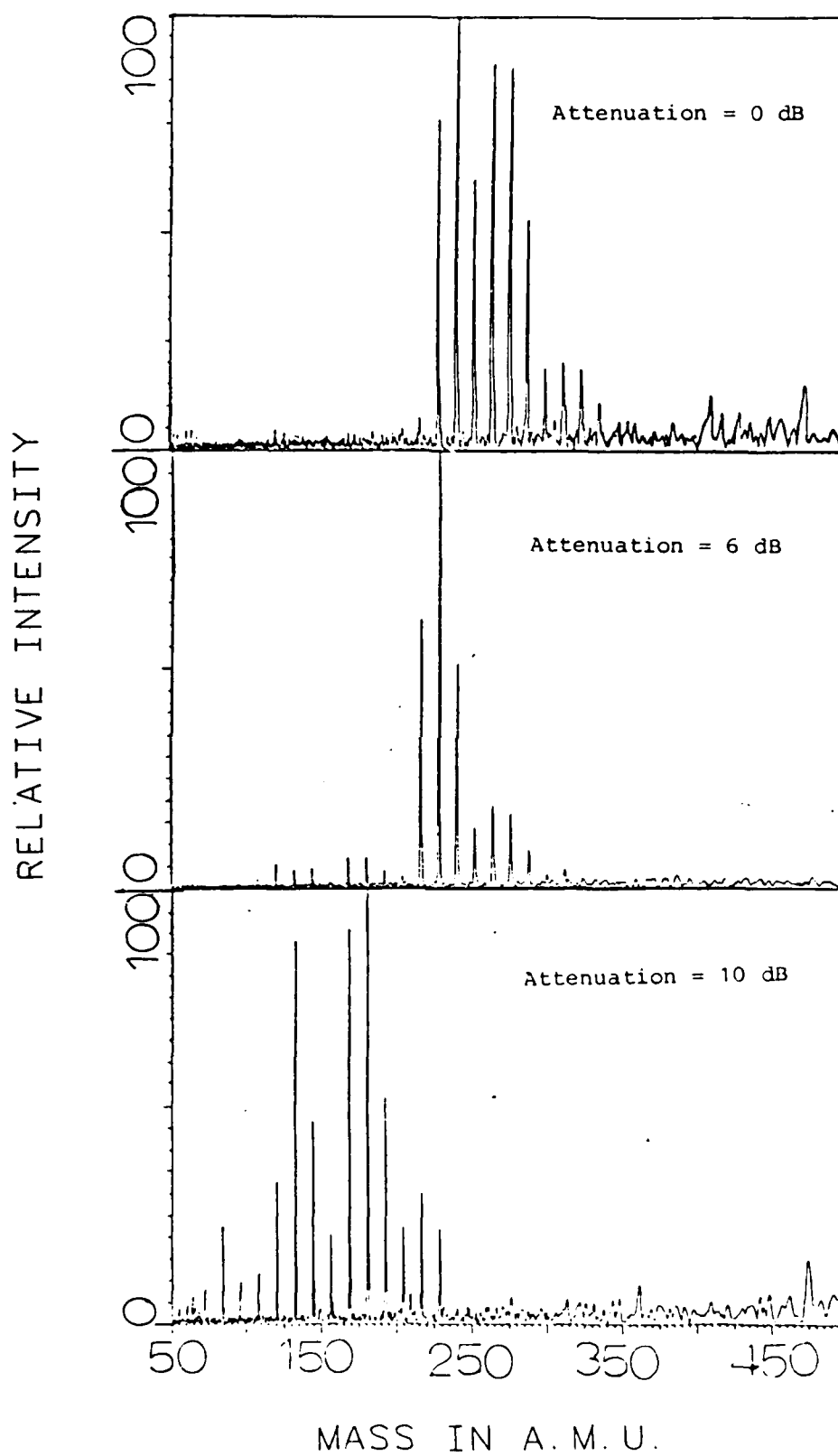


Figure 2

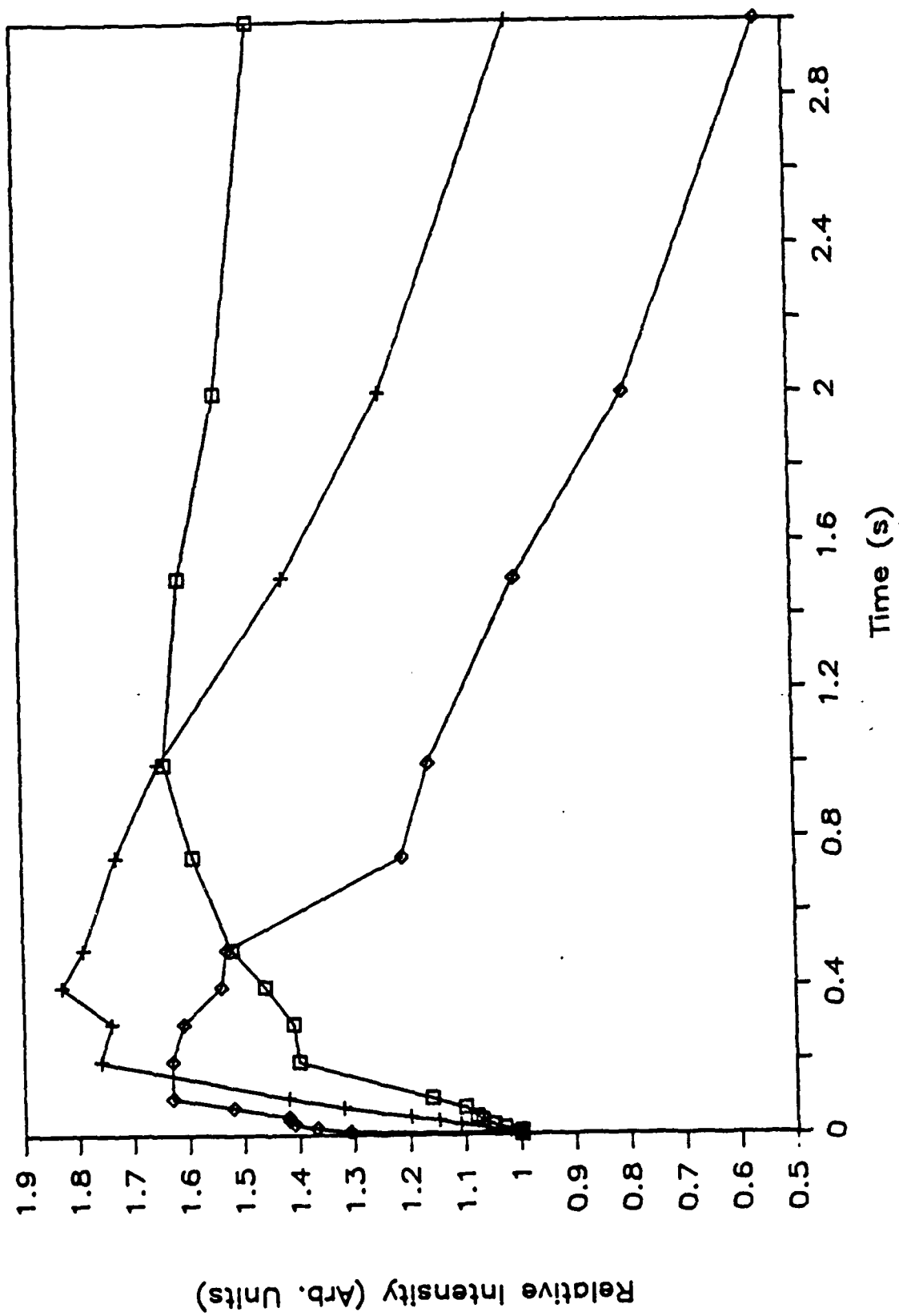


Figure 3

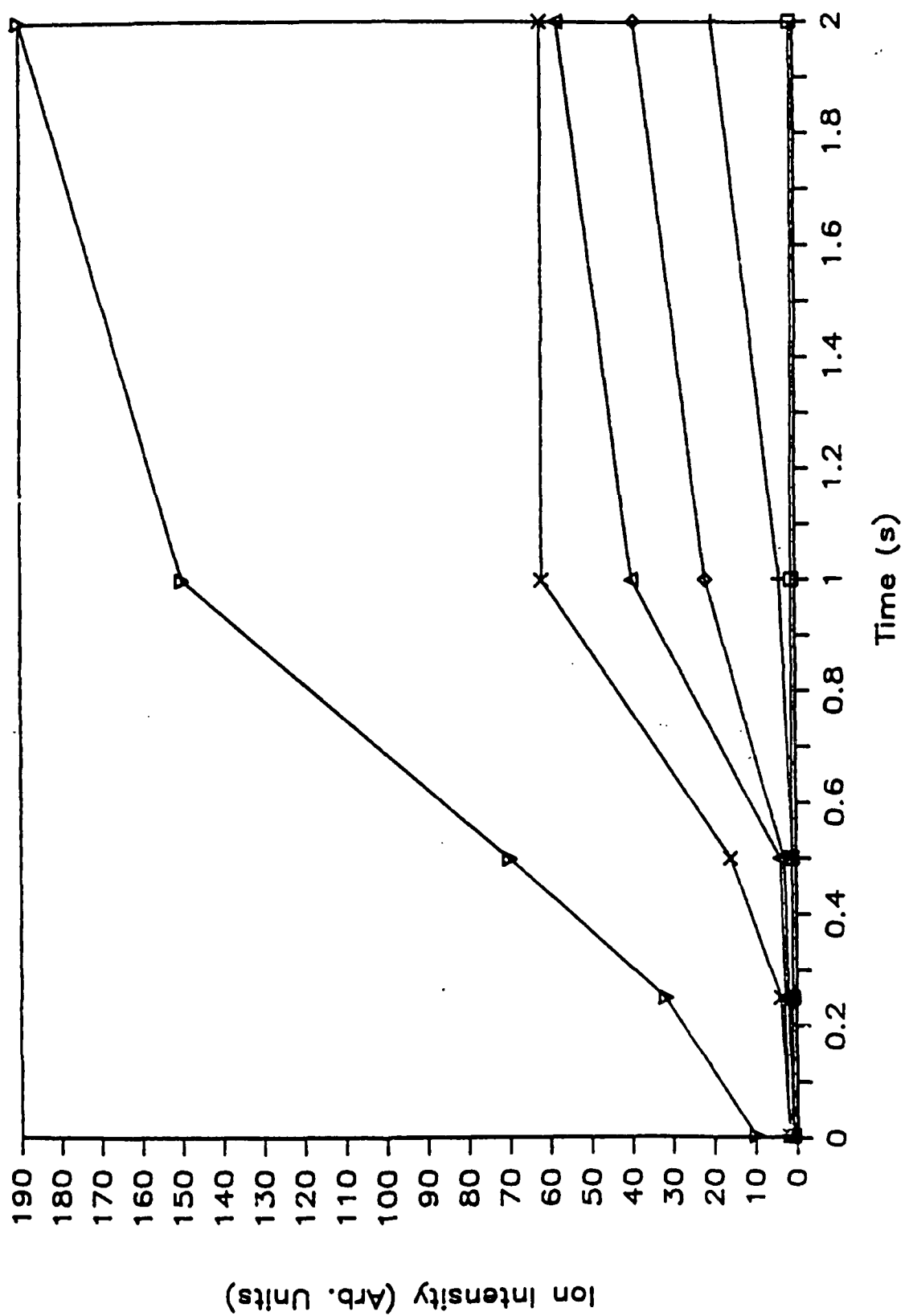
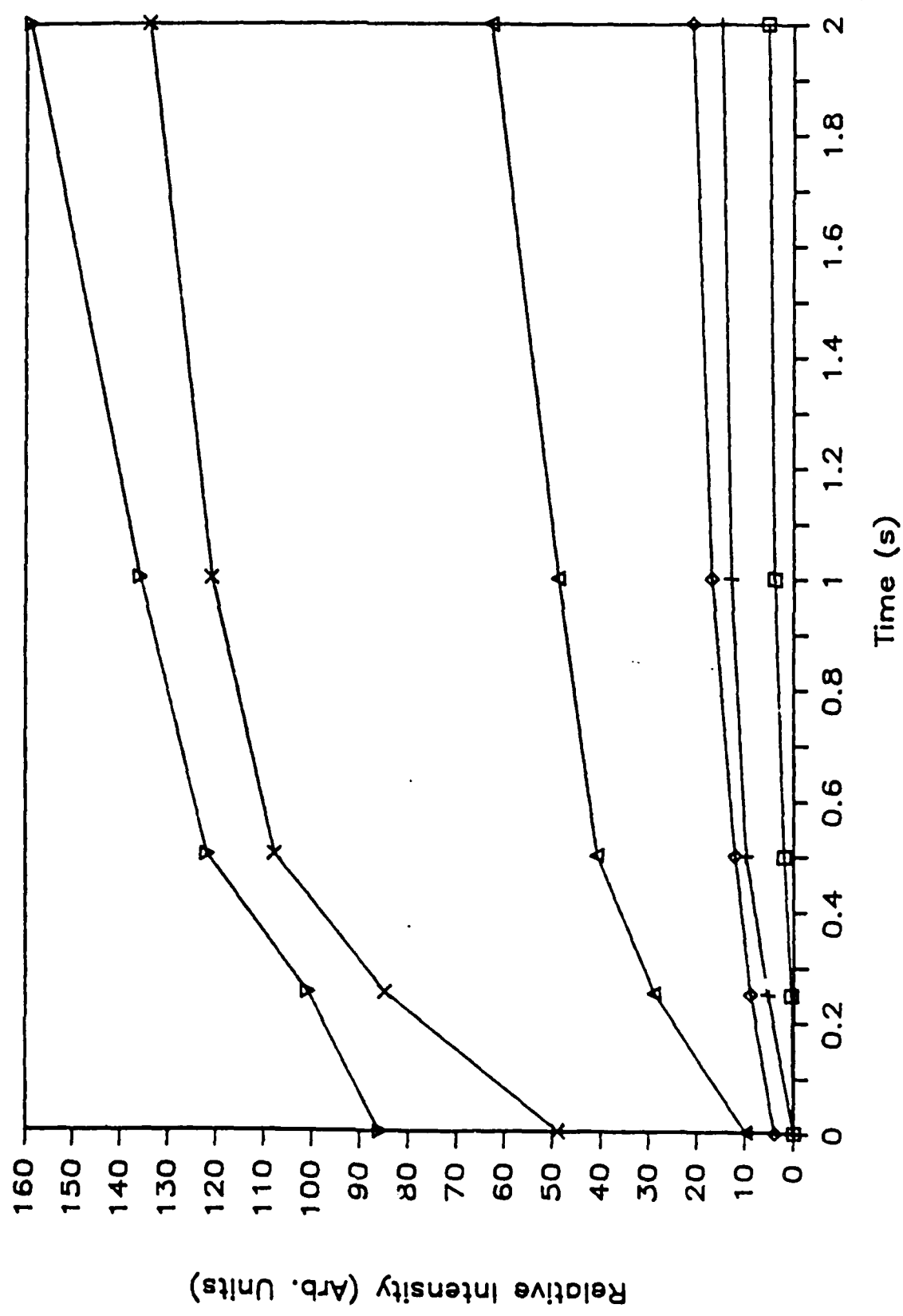


Figure 4



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